

### Experimental

**Preparation of  $\Delta^5$ -17-Ethynylandrostenediol-3,17.**—Purified and dried acetylene was bubbled through 50 cc. of dry ether in a flask with a mercury-sealed stirrer for one-half hour. Solutions of 1 g. of potassium in 15 cc. of dry tertiary amyl alcohol, and of 1 g. of dehydroandrosterone in 50 cc. of dry ether and 5 cc. of dry benzene were added dropwise during one-half hour, and stirring continued for five hours longer, acetylene being bubbled through the reaction mixture during the whole period and the reaction flask being maintained at room temperature. The reaction mixture was then acidified with saturated ammonium chloride solution containing a little hydrochloric acid and thoroughly extracted with ether. The ether was washed, dried over sodium sulfate, and evaporated under reduced pressure. The last traces of alcohol were removed in a stream of carbon dioxide. The residue was crystallized twice from methanol or aqueous methanol; yield 80–85%; m. p. 240–242°,  $[\alpha]^{25D} -119^\circ$  (chloroform).

Besides avoiding the use of liquid ammonia, this method has several other advantages over the methods of Ruzicka and Hofmann<sup>1</sup> and Kathol, *et al.*<sup>2</sup> The reaction time is less, and the use of Girard's ketone reagent for removing dehydroandrosterone is unnecessary.

**Preparation of  $\Delta^5$ -Pregnenediol-3,17-one-20 (III).**—A mixture of 800 mg. of  $\Delta^5$ -17-ethynyl-3,17-androstenediol (II), 1 g. of mercuric sulfate and 15 cc. of distilled water, previously boiled to remove oxygen, was heated in a sealed tube at 110–120° for twenty-four hours. The tube's contents were thoroughly extracted with ether, the ether washed with dilute sodium carbonate solution and water, dried over sodium sulfate and evaporated to dryness. The residue was crystallized from acetone, yield 10%.

After two recrystallizations the melting point was constant at 276–278°;  $[\alpha]^{25D} -106^\circ$  (dioxane).

*Anal.* Calcd. for  $C_{21}H_{32}O_3$ : C, 75.85; H, 9.71. Found: C, 76.11; H, 9.90.

The aqueous layer containing a precipitate was made alkaline with sodium hydroxide and thoroughly saturated with hydrogen sulfide. The next morning the mixture was extracted with ether and worked up as before, giving 180 mg. of product. After standing for several days 50 mg. more of the product was obtained in the same way; total yield 35%.

**Oxime of  $\Delta^5$ -Pregnenediol-3,17-one-20.**—From 30 mg. of  $\Delta^5$ -pregnenediol-3,17-one-20 the oxime was prepared in the usual manner; recrystallized from aqueous methanol or chloroform, m. p. 245–246°.

*Anal.* Calcd. for  $C_{21}H_{33}O_3N$ : C, 72.56; H, 9.58. Found: C, 72.63; H, 9.37.

### Summary

$\Delta^5$ -17-Ethynylandrostenediol-3,17 has been prepared, without recourse to liquid ammonia, by condensing acetylene and dehydroandrosterone in the presence of potassium tertiary amylate at room temperature.

$\Delta^5$ -Pregnenediol-3,17-one-20 has been prepared from  $\Delta^5$ -17-ethynylandrostenediol-3,17 in one step by the addition of the elements of water in the presence of mercuric sulfate. This provides a method for changing a member of the androstane series into a pregnane derivative with a ketone group at carbon atom 20.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

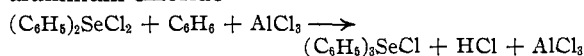
## A Synthesis of Aryl Sulfonium Salts

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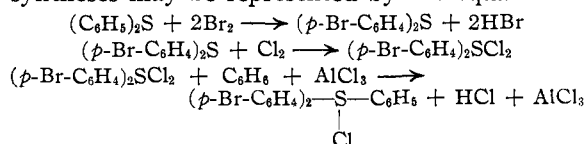
Sulfonium compounds in which all three hydrocarbon radicals are aryl in nature have not been prepared by the direct method of adding an aryl halide to an aryl sulfide. The usual methods of obtaining these compounds have involved the condensation of a sulfoxide with a hydrocarbon or derivative in the presence of sulfuric acid or aluminum chloride. In some cases the sulfoxide was not used as starting material but was formed in the course of the reaction.<sup>1</sup>

Leicester and Bergstrom<sup>2</sup> were able to form aryl selenonium compounds by the interaction of

diphenyl selenide dichloride with benzene and aluminum chloride

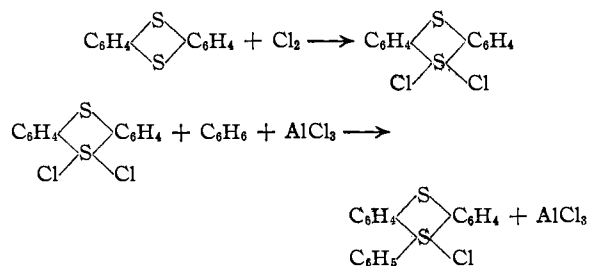


A search of the literature failed to disclose any attempt to use this method in the preparation of sulfonium compounds. It was thought that the synthesis would have certain advantages in the preparation of halogenated aryl sulfonium salts, and those containing cyclic aryl sulfides. These syntheses may be represented by the equations



(1) Michaelis and Godchaux, *Ber.*, **24**, 757 (1891); Smiles and Le Rossignol, *J. Chem. Soc.*, **89**, 696 (1906); **93**, 745 (1908); Courtot, *Compt. rend.*, **200**, 1541 (1935).

(2) Leicester and Bergstrom, *THIS JOURNAL*, **51**, 3587 (1929).



Three new compounds were prepared in this way: phenyl-*bis*-(*p*-bromophenyl)-sulfonium chloride, thianthrene-phenyl chloride and thianthrene-phenetyl chloride. These compounds showed a tendency to solidify in the form of a glass rather than in clean-cut crystals, and this behavior is quite common among aromatic onium salts. They were quite soluble in chloroform and fairly soluble in water. The free base in the case of the compound from diphenyl sulfide was alkaline to litmus paper and attacked slightly both aluminum and zinc. The salt seemed to be stable but the free base slowly decomposed on standing or heating with the liberation of phenol.

### Experimental

**Phenyl-*bis*-(*p*-bromophenyl)-sulfonium Chloride.**—Ninety grams of bromine was added gradually with shaking to 50 g. of diphenyl sulfide in 300 cc. of glacial acetic acid. The mixture was warmed on the water-bath for two hours. Dibromodiphenyl sulfide separated on cooling; it was filtered, washed with water, dried and recrystallized from glacial acetic acid.

Twenty grams of the sulfide was dissolved in 150 cc. of dry benzene, the solution cooled to 0° and chlorine was passed in until the formation of the orange red crystals of the dichloro addition compound appeared to be complete. The crystals were washed by decantation with two 50-cc. portions of ice-cold benzene. To a suspension of the crystals in 150 cc. of cold benzene, 8.5 g. of anhydrous aluminum chloride was added in small portions. The red crystals disappeared and a black liquid formed which was insoluble in the benzene. The reaction mixture stood for three hours at room temperature and then was heated to 80° for three hours. It was then cooled and decomposed with 100 cc. of 10% hydrochloric acid. The benzene layer was discarded and the aqueous layer extracted with chloroform several times. The chloroform extracts were dried with anhydrous sodium sulfate, and evaporated in a vacuum desiccator. Much frothing occurred but the residue finally took the form of glassy bubbles which were broken up with a stirring rod to a white powder. The powder could not be

crystallized successfully and gave no satisfactory melting point. The yield was 9.7 g., 36.6% of theory based on the dibromodiphenyl sulfide. This material when treated with chloroplatinic acid in water solution gave a buff colored precipitate. A platinum determination gave 15.53%; calculated for the double salt,  $\text{C}_{26}\text{H}_{26}\text{Br}_2\text{Cl}_2\text{S}_2$ , Pt 15.6%.

The sulfonium bromide and iodide were precipitated from a water solution of the chloride on addition of sodium bromide and sodium iodide solutions. The sulfonium hydroxide was prepared by boiling a solution of the chloride with freshly precipitated silver oxide for several hours. The solution of the hydroxide was strongly alkaline to litmus and attacked slightly both zinc and aluminum. The hydroxide was not obtained in the free state due to decomposition when the solution was evaporated.

**Thianthrene-phenyl Chloride.**—Thianthrene dichloride was prepared by passing chlorine into an ice cooled solution of 20 g. of thianthrene in 400 cc. of benzene. After adding 150 cc. of carbon disulfide and 100 cc. of benzene to the cooled flask containing the dichloride in suspension, 15 g. of anhydrous aluminum chloride was added sufficiently gradually so that the reaction was always moderate. The reaction mixture was stirred and allowed to come to room temperature over a period of two hours. It was then heated to boiling for three hours, cooled and decomposed with 10% hydrochloric acid. The water-hydrochloric acid layer was extracted with chloroform until it failed to give a precipitate with chloroplatinic acid. The chloroform extracts were evaporated and the sulfonium salt left as a white, rather amorphous appearing solid; yield 30%. A buff-colored double salt was obtained by treating a water solution of the sulfonium salt with chloroplatinic acid. This salt yielded 19.37% platinum on analysis. Calcd. Pt for  $\text{C}_{26}\text{H}_{26}\text{S}_4\text{Cl}_6\text{Pt}$ , is 19.51%.

**Thianthrene-phenetyl Chloride.**—The procedure was the same in general as the above: 20 g. of thianthrene, 20 g. of phenetyl and 26 g. of aluminum chloride were used. Due to the violence of the reaction it was necessary to add the aluminum chloride very gradually while keeping the reaction flask cooled with an ice-salt mixture. The white sulfonium compound isolated in the usual way gave a double salt with chloroplatinic acid. Calcd. for  $\text{C}_{40}\text{H}_{34}\text{Cl}_6\text{S}_4\text{O}_2\text{Pt}$ ; Pt, 18.2. Found: Pt, 18.05.

### Summary

The preparation of three new aryl sulfonium salts was described. The method used was based on the Friedel-Crafts synthesis and involved the reaction of a dichloro addition compound of a sulfide with an aromatic hydrocarbon or derivative.

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